DESIGN INVESTIGATION FOR THREE-DIMENSIONAL UNIFORMITY OF THE MASS TRANSPORT FIELD

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Abstract

CVD systems require extensive engineering to produce uniform mass transport distribution across the surface of the substrate. In reactors subject to viscous flow effects, design for manufacturing any particular product involves modelling and experimentation particular to the geometrical configuration. Pulsed-Pressure CVD (PP-CVD) accomplishes both the bulk mass transport and uniform precursor concentration through critically rapid expansion of the precursor into the evacuated chamber. The PP-CVD reactor mass transport system was studied through experimental investigation and parameter modelling. A modified naphthalene sublimation technique was employed in an isothermal low pressure reactor to determine 3D flow field convective and pressure conditions. Uniformity of the mass transport field was investigated for various geometries over a wide range of steady and pulsed pressure conditions using nitrogen gas. The results define the design envelope and processing regime in which convective uniformity is achieved by domination of expansion effects over viscous effects.

INTRODUCTION

The fundamental principle of chemical vapour deposition (CVD) is quite simple; reactant vapor or gas in the vicinity of a heated substrate react at the surface to produce a solid and volatile products. However, as Hitchman illustrates in his famous diagram of multi-dimensional system complexity, the engineering of reliable manufacturing equipment is a considerable challenge (1). The degree of complexity is reduced in low pressure reactors where viscous flow effects are negligible. However, many processes require a higher deposition rate than can be achieved at low pressures. The optimal CVD process would be mass transport limited with controllable and uniform precursor flux in three dimensions, high conversion efficiency, and geometric and size scalability.

We have been pursuing the idea of pulsing the reactor pressure as a means to achieve controlled uniform molecular flux (2). In our first investigations we found that the pulsed-pressure MOCVD of TiO_2 was accomplished at high conversion efficiency, and with good microstructure control (3). More recently, we have investigated the flow dynamics in the pulsed-pressure reactor, and reported that the rapid expansion of a gas into the reactor produced a uniform and well mixed flow pattern compared to steady flow (4). In current work we are studying the design relationships and processing parameters that produce a uniform pulsed flow field. The theory is based on the simplified model of

the injection and exhaust phases, and gives rise to the important non-dimensional parameters. The experimental method uses the relative sublimation of naphthalene samples placed throughout the reactor volume over the range of each non-dimensional parameter. The convective mass transport field uniformity is determined from a statistical treatment of the naphthalene sublimation data.

The most important non-dimensional parameters governing flow field uniformity in pulsed-pressure CVD are the exhaust time constant and the fill time constant. As long as the pulse cycle time and injection time were kept within specific ranges related directly to the design variables of reactor geometry and vacuum pump speed, then the convection field remained uniform up to the highest pressures studied, in excess of 20 kPa.

DESIGN OF PULSED PRESSURE CVD

The operating principle of pulsed-pressure CVD is a very rapid injection of the precursor into a low pressure reactor, followed by an evacuation cycle. This process produces a reactor pressure pattern shown in Figure 1, and is accomplished for gas precursor injection by the design shown as a schematic in Figure 2. The system can be broken down into three subsystems; injection, reactor and exhaust. The injection system consists of the gas source, usually a large high-pressure cylinder with supply pressure, P_s, controlled by a regulator, an injection supply volume, V_s, and timed solenoid valves to alternately fill the supply volume, and open the supply to the reactor to discharge the precursor injection through the orifice of area, A_s. The injection time, t_i, is controlled by a computer program, as is the total cycle time between injections.

Table 1. Design variables for Pulsed-CVD

Parameter	**Name**	**Range**
Injection Parameters:		
Supply Pressure	P_s	100-400 *kPa*
Supply Volume	V_s	1 – 5 *l*
Supply Tube Throat	A_s	1-10 mm^2
Injection Time	t_i	0.1 – 4 *sec*
Reactor Parameters:		
Reactor Volume	V_R	4.4 & 18.42 *l*
Peak Pulse Pressure	P_{max}	0.5 – 50 *kPa*
Min Pulse Pressure	P_{min}	10 – 300 *Pa*
Ultimate Pressure	P_u	7 *Pa*
Pulse Cycle Time	t_p	5 – 50 *sec*
Substrate Heater		Single Wafer
Evacuation Speed	S_R	$Q_pC/(C+Q_p)$
Reactor Conductance	C_R	$C_R >> C$
Exhaust Parameters:		
System Conductance	C	0.5-0.8 *lit/sec*
Pump Speed	Q_p	2.6 *lit/sec*

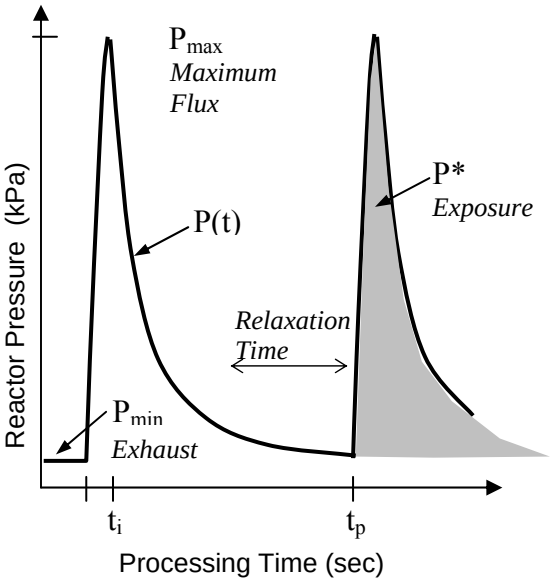

Figure 1. Reactor pressure during one pulse cycle, where the exposure, P*, is the integral of pressure from t = 0 to t_p.

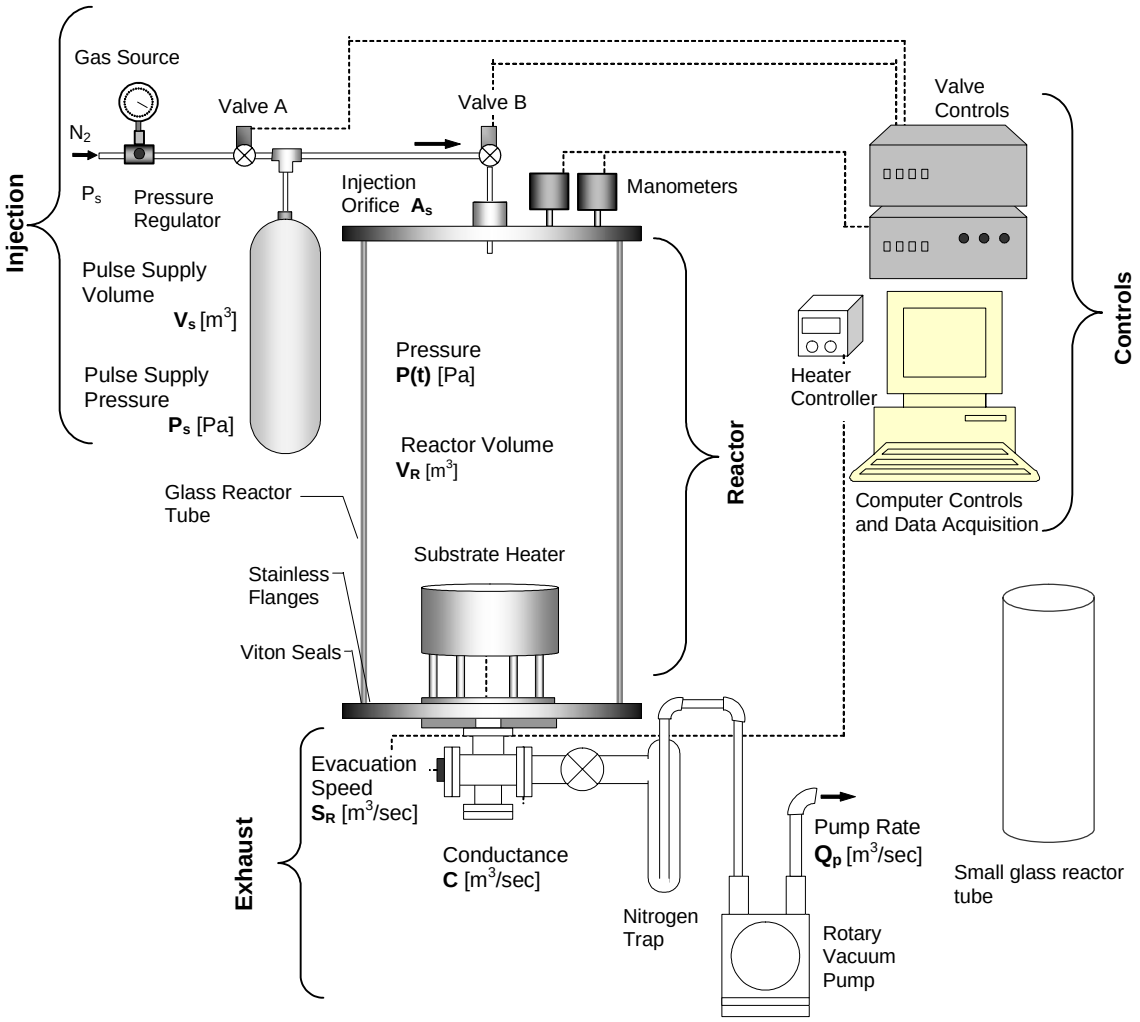

Figure 2. Schematic diagram of the experimental set-up showing the primary design subsystems for control of injection, reactor, and exhaust.

A production system would be designed for a given product according to the size and geometry of the substrate. Thus the size of the reactor is set by whether a thermal barrier coating is being deposited on a microturbine, or whether an insulating thin film is being deposited on 20 wafers. Once the reactor size, V_R, is fixed, then the design problem is to provide the reactor geometry, exhaust system, injection system, precursor flux and process timing uniformly over the substrate surface. The design and process variables for the system are listed in Table 1 and shown on Figure 1. If we neglect the exhaust mass flow rate during the injection time, then the pressure in the reactor, P(t), can be scaled by the minimum pressure, P_{min}, and the supply pressure, P_s, and is represented by:

$$\frac{P(t) - P_{\min}}{P_s} = \frac{V_s}{V_R}\left(1 - \exp\left(\frac{-t}{\tau_s}\right)\right) \qquad \textit{for t from 0 to } t_i \qquad [1]$$

Where the injection time constant, τ_s, is the ratio of the source discharge rate, which is sonic choked flow, and the source volume. The source discharge rate, C_s, is primarily a function of the injector orifice cross section area, A_s:

$$\tau_s = \frac{V_s}{C_s} = \frac{V_s}{RTA_s / c^*} \qquad [2]$$

Where R is the gas constant, T is the source temperature and c* is the characteristic velocity for the gas. At time t_i the injection valve is closed, the reactor has reached a pressure of P_{max}, and the rest of the cycle is a pump-down to the minimum pressure. The reactor pressure during the exhaust phase can be scaled and represented as:

$$\frac{P(t)-P_{\min}}{P_{\max}-P_{\min}} = \exp\left(-\frac{t}{\tau_R}\right) \qquad \textit{for t from } t_i \textit{ to } t_p \qquad [3]$$

In this phase of the pulse, the important operating parameter is the evacuation time constant, τ_R, which is the ratio of the reactor volume, V_R, and the evacuation speed, S_R, which depends on vacuum pump speed, Q_p, and the exhaust system conductance, C:

$$\tau_R = \frac{V_R}{S_R} = \frac{V_R}{\left(\frac{Q_P C}{Q_P + C}\right)} \qquad [4]$$

The film nucleation rate and growth rate are determined by the maximum pressure and by the total *exposure* to molecular flux, obtained from the integral of the pressure over the pulse (5). Composition purity is affected by the minimum *exhaust* pressure. Crystal growth will be greatly influenced by the *relaxation time* between precursor exposure cycles (6). The important deposition parameters, P_{max}, P_{min} and cycle time, are relatively straight forward to control in the small reactor. A very rapid pressure rise has been accomplished by injecting a set volume of liquid precursor through an ultrasonic atomizer, with the flash evaporation causing the sharp pressure spike (7). In the present study we are studying the flow field when a gas precursor is injected, and engineering the system for the requirement of uniform molecular flux at the substrate. Uniformity of the convection field, and how it relates to the injection and cycle timing, reactor and supply volumes, and injection and exhaust rates must be determined experimentally.

Rapid expansion of a gas into a low pressure vessel will produce a well mixed, highly turbulent flow pattern. In order to produce this phenomenon, we need rapid injection and we need to wait long enough before the next injection for the reactor to return to P_{min}. From Eqn. 3, if the pulse time is at least four times the exhaust time constant, then the reactor pressure will be within 98% of reaching P_{min}. From Eqn. 1, if the injection time is around a tenth of the injection time constant, then the fill is essentially an instantaneous expansion, that is $(P(t_i)-P_{min})V_R \sim P_s V_s$. Given this reasoning, we examined the uniformity data as a function of the ratio of the pulse time to the injection time, expecting that the flow field would have the well mixed behavior when t_p/t_i >20-40 with the exact value to be found from experiment for a given geometry.

$$\frac{t_p/\tau_R}{t_i/\tau} = \frac{t_p}{t_i}\frac{\tau_s}{\tau_R} = \frac{t_p}{t_i}\cdot\frac{V_s}{V_R}\frac{S_R}{C_s} \geq n \qquad [6]$$

Eqn. 6 gives the rationale for the empirical determination of the design and operation range from experimental measurement of desired system performance parameters. We propose that if the expansion pressure rate of change is rapid enough, that the expansion effects will dominate over the development of viscous flow patterns. The key measure of performance will be flow uniformity, and the relationship between reactor geometry, pump speed, and operating timing can be determined by determining the range of *n* for good uniformity.

EXPERIMENTAL METHOD

We devised a method to measure the relative mass transport uniformity in the reactor chamber. Small cylinders of naphthalene were cast and suspended from a slender wire frame throughout the volume of the reactor as shown in Figure 3. The specific sublimation rate of each cylinder depends on temperature, pressure and the convection mass transport field. Uniform convection and concentration fields throughout an isothermal reactor, would result in the same specific sublimation rate for all samples. The graph in Figure 3 shows sublimation measurements for six samples at constant pressure with no reactor flow. With this result being a measurement of uniformity = 1, then the measurement accuracy is ± 0.02mg/sec·mm^2. Experiment time was set so that the error in the mass sublimation measurement from loading and weighing was less than 2%.

The specific sublimation rate, $\dot{S}_i$ [mg/sec·mm^2], for each naphthalene cylinder is easily calculated from the mass loss divided by that cylinder's surface area, and the total experiment time. The convective uniformity, U, for M naphthalene samples placed at positions throughout the reactor taking into account not only the average sublimation, $\bar{\dot{S}}$, but also the total magnitude of the sublimation is given as:

$$U = \frac{\sum_{i=1}^{M} \dot{S}_i - \sum_{i=1}^{M} \left| \dot{S}_i - \bar{\dot{S}} \right|}{\sum_{i=1}^{M} \dot{S}_i} = 1 - \frac{\sum_{i=1}^{M} \left| \dot{S}_i - \bar{\dot{S}} \right|}{\sum_{i=1}^{M} \dot{S}_i} \qquad [5]$$

If all samples have the same specific sublimation rate, regardless of the absolute magnitude, then the uniformity will have a value of unity. If some samples have very

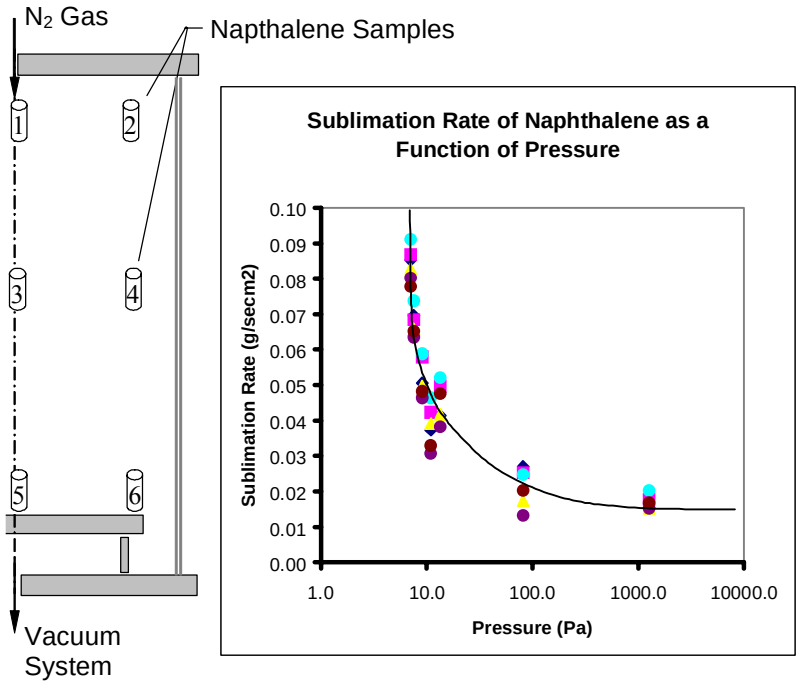

Figure 3. Naphthalene measurement arrangement and calibration data of specific sublimation of individual samples at fixed pressure.

high sublimation while others sublime slower than the average, then the uniformity will have a low value. In principle, the range for the uniformity measure would be $\mathbf{0} \le \boldsymbol{U} \le \mathbf{1}$, although several orders of magnitude difference in sublimation is needed to get vanishingly small uniformity. This measure was used to study the uniformity of the convection field over the range of design and operation parameters.

Materials science research using small coupons will determine a peak pressure, P_{max}, exhaust minimum pressure, *exposure*, P*, and *relaxation time*, t_p, for a desired thin film. These parameter will then be used to design the industrial scale system.

$$P^* = \frac{AB}{t_p} \int_{P_{min}}^{P_{max}} P(t)dt \qquad [7]$$

Where AB is the concentration of the reactant A in the bulk gas B, the integral is over one pulse, and the pressure is described by Eqn. 3. Uniformity experiments provide an upper limit on P*. A production process will be optimized for maximum through-put. In pulsed-pressure CVD, this could be accomplished by increasing the pulse rate, and by increasing the peak pressure. However, the processing rate must be balanced with the quality of the product which will depend on uniformity and on P*. For stable operation (e.g. $t_p > 4\tau_R$) the exposure is directly related to the maximum peak pressure.

RESULTS

The convective uniformity was measured for more than fifty experiments with three different reactor volumes and several different injection and exhaust configurations. The pulse cycle timing relation predicted from Eqn. 3 was verified for all cases. When the pulse timing is at least four times the reactor pump-down time constant, then the system operates in a stable, repeatable manner, and the uniformity throughout the reactor is very high, consistently above 0.95. In addition, if the top 1/4 of the reactor volume is exempted from the uniformity measure, and left to act as a flash expansion zone, then the uniformity of the remainder of the reactor volume is above 0.9 for t_p/τ_R as low as 3.

Figure 4 shows the uniformity results for experiments of 30 minute duration in two different size reactors. All experiments showed excellent uniformity (>0.95) for the shortest injection times and pulse times at least $4\tau_R$. The data indicate that uniformity greater than 0.95 can be achieved for t_p/t_i ratio above 20 for the small reactor and t_p/t_i greater than 40 for the large reactor. Both reactors had the same pump and exhaust system, but different injection supply volume and orifice area. In both cases, the range for high uniformity is characterized by very sharp pressure spikes and return of the reactor pressure to P_{min} during each cycle.

Figure 5 shows the uniformity results as a function of the peak reactor pressure for experiments with $t_p/t_i > 20$. The figure also shows for reference some uniformity measurements at steady flow pressures with exposure equal to the pulsed exposure in Eqn. 7. At pressures in the range of 16 kPa, the uniformity is slightly reduced, but the uniformity is always significantly above that for steady flow conditions.

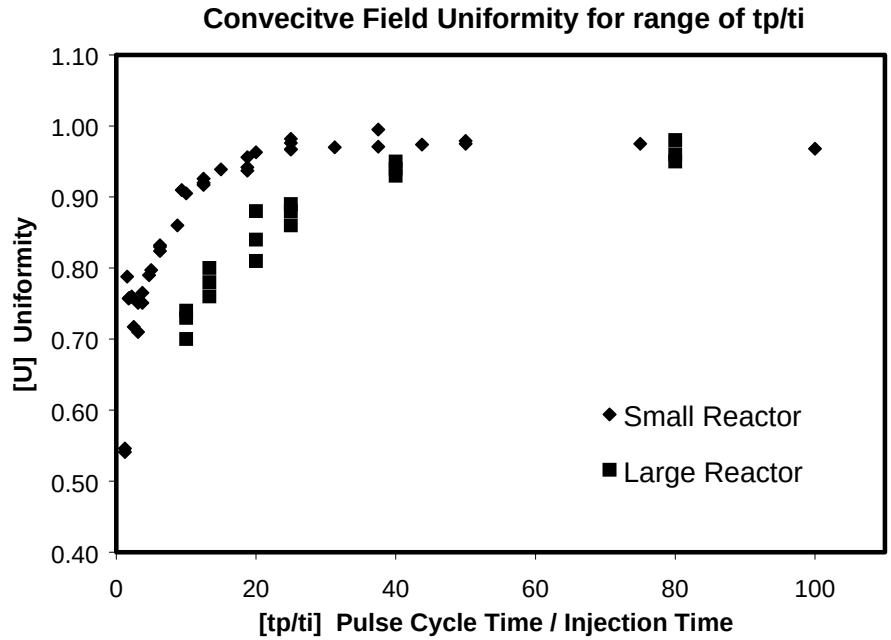

Figure 4. Empirical relation for both large and small reactor, both with the same vacuum pump and exhaust configuration. A wide range of pulse peak pressures is represented.

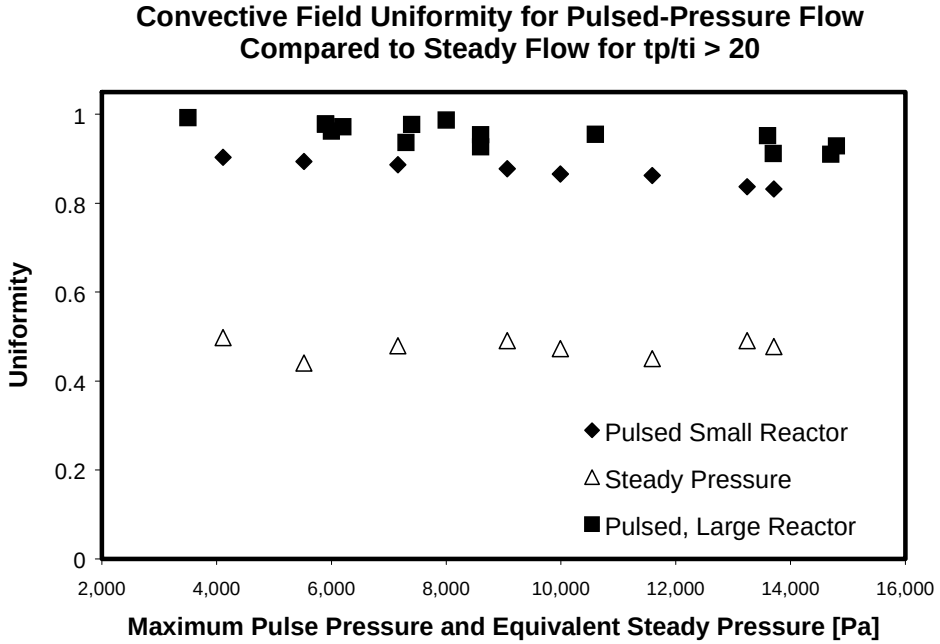

Figure 5. Experimental results of naphthalene sublimation uniformity measured for 30 minute duration experiments over the range of pulse cycle time and injection time. A wide range of maximum and minimum pulse pressure are represented, up to 16 kPa.

CONCLUSION

Carrying on the pioneering work of Professor Rishi Raj at Cornell and UC Boulder, we have investigated the phenomena of mass transport uniformity in pulsed-pressure CVD, and determined the design relations for scaling materials research processes to production scale equipment. This study describes the primary processing variables of pulse cycle time and injection time, and how they are related to reactor system design variables for gas source CVD. The primary design variables are supply volume, reactor volume, injection orifice size and exhaust pump rate. Simple relations are presented which represent the gas expansion rate, both during the injection and exhaust portions of the pulse cycle. The range of operation for a given reactor size is proposed where the expansion effects dominate the mass transport processes, producing a highly mixed, uniform concentration field without velocity field due to viscous flow development. Expansion effects dominate when t_p/t_i, the ratio of injection time and pulse time, is greater than 20.

We have developed a naphthalene sublimation technique and an analysis method to assess the mass transport uniformity throughout the reactor. The specific sublimation rate of small cylinders placed throughout the reactor volume are compared in a statistical manner to arrive at a uniformity measure which ranges from 0 to 1. The uniformity measurements verified the proposed model of expansion dominated mass transport. In addition, the uniformity was measured for a range of peak pressures while operating in the expansion dominated regime. Up to the limits of our current set-up, the mass transport field uniformity was maintained above 0.85 for peak pressure up to 16kPa. The pulsed-pressure uniformity was at least twice as good as for uniform flow at an equivalent molecular exposure rate.

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